

Application of photosensitive surfactant based on natural rubber in emulsion polymerizations

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Summary

Photosensitive surfactant was prepared by incorporation of maleic anhydride to natural rubber, followed by introduction of cinnamate groups and neutralization of the remaining carboxylic groups. The surfactant was used in emulsion polymerization of styrene and acrylic monomers, giving rise to stable reactive emulsion. Coated onto HDPE, this emulsion lead to solid films which were submitted to UV irradiation.

Introduction

The increasing concern with respect to environmental control has restricted the use of organic solvents in favor of aqueous systems. These systems make use of a non-flammable, non-toxic, cheap solvent, allowing a better control of the viscosity, easier cleaning of the equipments, and preparation of films with reduced thicknesses. Potential applications include wood lacquer, paper varnish, inks, and coatings for plastics (1).

Photocurable aqueous compositions may consist of aqueous dispersions or solutions. Basically, dispersions and emulsions are prepared from different oligomers or polymers, surfactants and photoinitiators. When conventional surfactants are used in emulsion polymerizations, some problems are observed. In order to obtain stable latexes, surfactants are added in amounts large enough to generate a great number of polymerization sites. Very often, more surfactant is added at the end of polymerization to assure a colloidal stability to the particles formed. This excess, after application and drying of the latex, will not be uniformly distributed among the coalescent polymeric particles. In fact, surfactant molecules migrate to the surface giving rise to stains when exposed to atmospheric humidity (2).

In an attempt to minimize these negative aspects, reactive surfactants have been developed which, through vinyl polymerization are hindered from moving to the surface (3).

In this work, photosensitive emulsifier derived from natural rubber was prepared and employed in the emulsion polymerization of styrene and acrylic monomers.

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Experimental

Natural rubber was coagulated from the latex by adding 2% v/v acetic acid, washed with water and dried in an air-oven, at 50°C. The dried rubber was then mastigated in a two-roll mill during 30 minutes at room temperature.

After purification by dissolution in benzene, followed by precipitation in methanol, the viscosimetric molecular weight of the degraded rubber, determined in a Mettler-Toledo viscosimeter (Low - Shear 40), was found to be $2,24 \times 10^5$.

The adduct natural rubber/maleic anhydride (NR-MA) was obtained by adding two moles of the anhydride to each mole of isoprene units present in a solution of natural rubber in o-dichlorobenzene. The mixture was kept at 180-190°C for 12 hs, then poured onto n-heptane. The precipitate, with 35,6 mol% incorporation of maleic anhydride was dissolved in acetone and kept in refrigerator under nitrogen.

Photosensitive rubber used as surfactant was prepared by reacting the adduct NR-MA and 2-hydroxyethylcinnamate, as described previously, followed by neutralization with 0,5 N KOH methanolic solution (4).

Critical micellar concentrations, CMC, for the photosensitive surfactant (PS) as well as for an equimolar mixture of this surfactant and sodium lauryl sulphate (SLS) were obtained in a Dü Nouy tensiometer, at 60°C, according to the equation (5),(6):

$$\gamma = m.g / 2.L$$

where:

γ = surface tension (dyn/cm)

m = weight (g) for each standard

g = 980 cm/s²

L = circumference of the ring (cm)

Styrene and acrylic monomers were purified according to the literature and emulsion polymerized under various reaction conditions (7), as shown in Table 1.

Photosensitive emulsions were coated onto HDPE and dried to form solid films which were irradiated at 27°C with a 200 W high pressure mercury lamp (Ushio Electric, model UI-501). After irradiation the consumption of reactive group was followed by IR spectroscopy.

Results and discussion

Figure 1 shows surface tension versus concentration curves for aqueous solutions of both the photosensitive surfactant and sodium lauryl sulphate. From these curves, CMC values of 0.7% and < 0.1% were obtained for these surfactants.

Mixtures 1:1 (w/w) of the two surfactants were also prepared and the CMC value, 0.1%, for this system was given by the curve presented in Figure 2. This value, 0.1%, compared to 0.7%, found for pure PS, indicates that the mixture PS/SLS is more effective in micelle production.

Preliminary attempts to emulsion polymerize acrylic monomers by using PS alone lead to undesirable results. No polymerization was obtained. Moreover, emulsions with concentrations higher than 8% PS resulted unstable.

Table 1: Formulations used in emulsion polymerizations

Ingredient (weight %)	Formulation					
	A	B	C	D	E	F
Sodium lauryl sulfate	0.25	1.0	1.0	4.0	2.0	2.0
Photosensitive surfactant	2.5	7.5	10.0	7.5	7.5	15.0
Potassium persulfate	0.1	0.1	0.1	0.1	0.1	0.1
Sodium metabisulfite	0.1	–	–	–	–	–
Sodium bicarbonate	0.2	–	–	–	–	–
Sodium acid phosphate	–	0.1	0.1	0.1	0.1	0.1
Styrene	40	40	40	25	25	25
Butyl methacrylate	10	10	10	25	25	25
Water	to complete 100 parts					
Total	100					

Temperature: 70 - 80°C

Reaction time: varying from 15 to 280 minutes

The presence of styrene as comonomer gave rise to emulsions which were more or less stable depending on the initiator. Potassium persulfate/ sodium metabisulfite system was still inefficient in promoting stability. Changing to the system potassium persulfate/ sodium biphosphate, stable emulsions of varying compositions were obtained, as shown in Table 1, and the use of higher percentage of PS, formulation F, was also possible.

From formulation F films for irradiation were prepared by coating the obtained emulsion onto HDPE. The reaction progress was followed by IR spectroscopy, as can be seen in Figure 3.

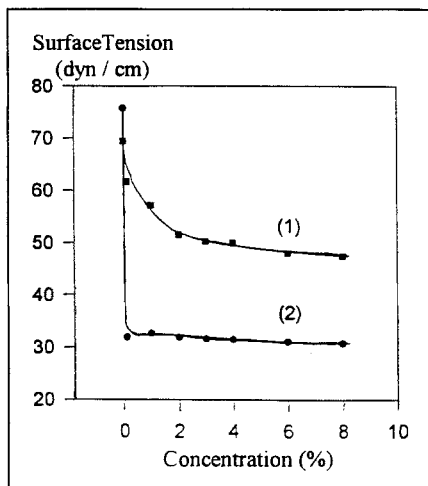


Figure 1: Surface tension versus concentration curves for aqueous solutions of the photosensitive surfactant (1) and sodium lauryl sulfate (2).

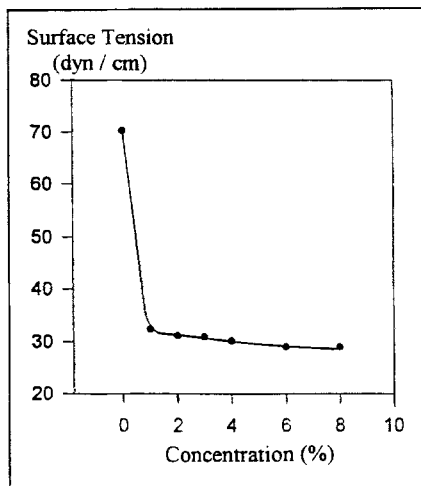


Figure 2: Surface tension versus concentration curves for aqueous mixtures 1:1 (w/w) of both surfactants.

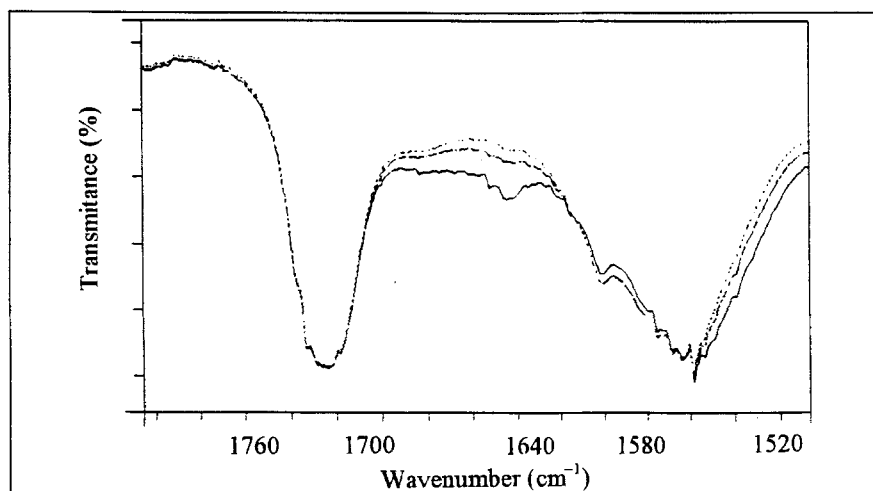


Figure 3: IR spectra taken after irradiation for (a) 0 min, (b) 20 min and (c) 60 min.

The spectra obtained after each irradiation time revealed decreases in the absorption at 1637 cm^{-1} , corresponding to C=C of cinnamate group. Since carbonyls do not participate in the photoreaction, the absorption at 1728 cm^{-1} was considered as reference. So, the consumption of cinnamate groups was estimated from the relative height of peaks at 1637 and 1728 cm^{-1} , as $A^{\text{rel}} = A_{1637} / A_{1728}$, as shown in Figure 4.

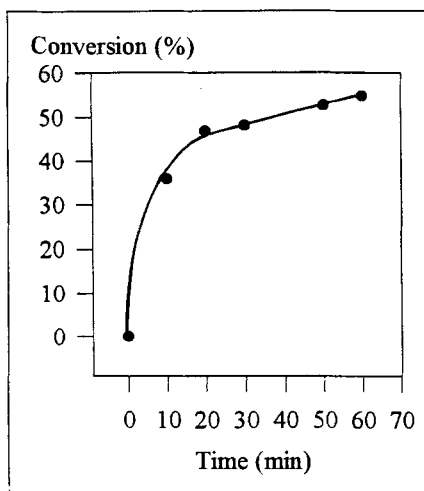


Figure 4: Conversion as a function of irradiation time.

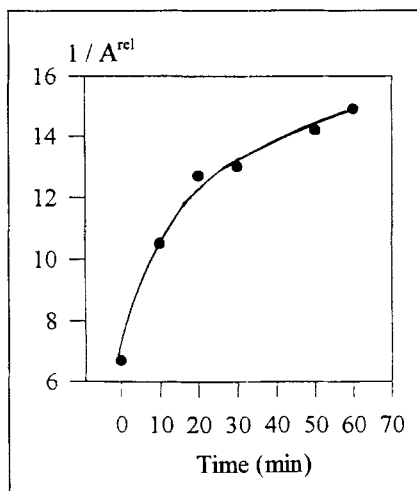


Figure 5: Dependence of $1 / A^{rel}$ on irradiation time.

The kinetics for the photodimerization of cinnamate groups bound to flexible chains had been already well established in former papers by Azuma et al. According to this author, during the irradiation of solid films no isomerization occurs and the reaction order will depend on the intensity of the absorbed light (8),(9).

However, more recently, studies on Araldite[®]-type polymers revealed a second order kinetics for the photodimerization reaction, what would be in accordance with a bimolecular character of a [2+2] cycloaddition. Also, it was taken into account the importance of cis-trans equilibrium during irradiation (10),(11).

Applying the same reasoning to the material under study, the curve shown in Figure 5 can be obtained.

Clearly, two straight portions are observed. The one appearing at the early stages of irradiation is due primarily to cis-trans isomerization. Then, the photoinduced dimerization would be represented by the second linear portion from which the rate constant, calculated as the slope, is $0,056 \text{ mol}^{-1} \text{ cm}^3 \text{ min}^{-1}$.

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